Using Chemical, Hydrologic, And Age Dating Analysis To Delineate Redox Processes And Flow Paths In The Riparian Zone Of A Glacial Outwash Aquifer-Stream System

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Abstract

A combination of chemical and dissolved gas analyses, chlorofluorocarbon age dating and hydrologic measurements were used to determine the degree to which biogeochemical processes in a riparian wetland were responsible for removing NO_3^- from ground waters discharging to the Otter Tail River in west-central Minnesota. An analysis of river chemistry and flow data revealed that NO_3^- concentrations in the river increased in the lower half of the 8.3 km study reach as the result of ground-water discharge to the river. Ground-water head measurements along a study transect through the riparian wetland revealed a zone of ground-water discharge extending out under the river. On the basis of combined chemical, dissolved gas, age date, and hydrologic results, it was determined that water chemistry under the riparian wetland was controlled largely by up-gradient ground waters that followed flow paths up to 16 m deep and discharged under the wetland, creating a pattern of progressively older, more chemically reduced, low NO_3^- water the further one progressed from the edge of the wetland towards the river. These findings pose challenges for researchers investigating biogeochemical processes in riparian buffer zones because the progressively older ground waters entered the aquifer in earlier years when less NO_3^- fertilizer was being used. NO_3^- concentrations originally present in the ground water had also decreased in the up-gradient aquifer as a result of denitrification and progressively stronger reducing conditions there. The resulting pattern of decreasing NO_3^- concentrations across the riparian zone may be incorrectly interpreted as evidence of denitrification losses there instead of in the up-gradient aquifer. Consequently, it is important to understand the hydrogeologic setting and age structure of the ground waters being sampled in order to avoid misinterpreting biogeochemical processes in riparian zones.

1. Introduction

Over the last two decades, there has been growing interest in the use of riparian buffer zones along river corridors to mitigate the effects of nonpoint-source pollution on water quality (Hill, 1996). Most early interest in riparian buffer zones focused on their ability to trap sediment and sediment-borne contaminants (Young et al., 1980; Dillaha et al., 1989; Vought et al., 1994), while recent interest has shifted to their ability to remove contaminants from ground water before it enters surface-water bodies (Groffman et al., 1992; Haycock et al., 1993; Gilliam, 1994; Jansson et al., 1994; Hill, 1996). The ability of riparian buffer zones to remove pollutants, particularly nitrate (NO_3^-), from ground water is related primarily to the presence of reducing conditions in the organic-rich, saturated sediments that commonly occur in riparian buffer zones. Nitrate removal in riparian buffer zones is important because (1) it poses human and ecosystem health risks (Mueller et al., 1995), (2) it is the most common nonpoint-source pollutant (Mueller et al., 1995), and (3) it is mobile in ground and surface water (Mueller et al., 1995). Under reducing conditions nitrate can be converted to N_2O and then N_2 gas by the microbially mediated process of denitrification (Korom, 1992):

$$5CH_2O + 4NO_3^- \rightarrow 2N_2 + 4HCO_3^- + CO_2 + 3H_2O \qquad (1)$$
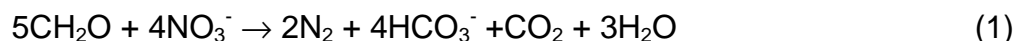
Studies of denitrification potential in riparian buffer zones increase our understanding of factors controlling this process and may allow us to predict when, where, and how riparian buffer zones will be effective nonpoint-source pollution controls.

Assuming NO_3^- is present, there are three basic requirements for denitrification: (1) a microbial denitrifier population, (2) low concentration of dissolved oxygen (O_2), and (3) a readily available source of C or a reduced inorganic species such as Fe^{2+}, Mn^{2+}, or S^{2-} to serve as an electron donor (Tiedje et al., 1982; Postma et al., 1991; Korom, 1992) following a reaction of the form:

$$10Fe^{2+} + 2NO_3^- + 14H_2O \rightarrow N_2 + 10FeOOH + 18H^+ \qquad (2)$$

In reactions (1) and (2), NO_3^- is converted to N_2 gas. Under most conditions, this N_2 gas will remain in solution until the ground water discharges to a surface-water body and equilibrates with the atmosphere (Heaton and Vogel, 1981; Blicher-Mathiesen, 1998). By measuring this excess N_2, it is possible to reconstruct, in effect, the amount of NO_3^- originally present in the ground water (Heaton and Vogel, 1981; Vogel et al., 1981; Wilson, et al., 1990; Smith et al., 1991; Bohlke and Denver, 1995; Blicher-Mathiesen et al., 1998; Modica et al., 1998). Most studies of NO_3^- removal by riparian zones have inferred denitrification losses based on measurements of the decrease in NO_3^- concentrations at several locations across the riparian zone, but few if any studies have measured nitrogen gas phases to verify that conclusion. Even fewer riparian zone studies have conducted a complete, simultaneous analysis of the various nitrogen species coupled with an analysis of the controlling hydrogeologic and biogeochemical processes involved, leaving many questions unanswered with respect to the true fate of

NO_3^-.

Hill (1996) provided a critical review of the current state of our knowledge concerning NO_3^- retention by riparian buffer zones. He concluded that previous research had failed to adequately consider hydrogeologic controls on biogeochemical processes and had been conducted in similar settings, making it difficult to extrapolate findings to other areas. These conclusions seem particularly relevant in light of recent studies that have shown that ground water may flow under riparian zones and discharge to streams without undergoing denitrification (Bohlke and Denver, 1995; Burt et al., 1999), or may take many decades to transit ground-water flow paths before discharging to surface waters (Modica et al., 1997, 1998).

In this paper, we examine the hydrogeologic and biogeochemical controls on the evolution of water chemistry at a site in west-central Minnesota. Previous work in the area examined nitrogen cycling in the 212 km^2 agro-ecosystem (Puckett et al.,1999) and hydrogeologic and biogeochemical processes controlling the transport and fate of nitrogen in an upland portion of the aquifer (Puckett and Cowdery, 2002). The Puckett and Cowdery (2002) study demonstrated a pattern of decreasing NO_3^- concentrations with both increasing depth and ground-water age along a representative 5 km flow system transect, and their modeling results predicted that ground water from deep in the aquifer should discharge at the terminus of the flow system in the riparian zone adjacent to the Otter Tail River.

The study reported here focused on the hydrogeology and biogeochemistry of the riparian zone where the original 5 km transect intersected the Otter Tail River (Figure 1). Examination of historical water quality data from for the Otter Tail River indicated that in spite of the large amounts of nitrogen entering the Otter Tail watershed (Puckett et al., 1999), little was being discharged in the river and almost none of that was in the form of NO_3^-. Our primary hypothesis in this study, therefore, was that denitrification was taking place in the riparian buffer zone, preventing NO_3^- contamination of the Otter Tail River. Within the context of this hypothesis, we evaluated the commonly reported occurrence that ground water flowing horizontally through the riparian zone as shown in Figure 2a, passes through progressively stronger redox environments, resulting in the loss of NO_3^- through denitrification. Denitrification losses, inferred by measuring changes in NO_3^- concentration at various points across the riparian zone, are frequently offered as evidence of this process. However, this approach has drawbacks since it is possible that by sampling along a transect through the riparian zone, investigators are merely observing a series of discharging ground waters of progressively greater age and stronger redox state, containing less NO_3^-. This pattern of decreasing NO_3^- concentration may occur because less fertilizer was applied in earlier years when the water originally recharged and (or) because denitrification occurred in the up gradient aquifer. Consequently, we also considered the alternative hypothesis that ground water from deeper and progressively more reduced portions of the up gradient aquifer were discharging in the riparian zone as shown in Figure 2b, thereby creating the appearance of NO_3^- loss in the riparian zone.

Although the chemistry of ground water sampled along the riparian transect may appear similar in each scenario, the two different flow paths should result in distinctively different patterns of water age with the deepest and longest flow paths shown in Figure 2b resulting in ground-water ages up to several decades older. Therefore one important criterion for evaluating these two hypotheses would be that there should be no significant horizontal age gradient across the riparian zone if ground water is moving horizontally as shown in Figure 2a, whereas there should be a gradient of increasing age across the riparian zone if ground water is discharging vertically as shown in Figure 2b.

2. Study Area

This study was conducted in Otter Tail County in west-central Minnesota, USA (Figure 1) in a 36 km^2 subunit of the Otter Tail outwash aquifer north of the Otter Tail River near Perham. The Otter Tail outwash aquifer consists mostly of fine to coarse, fairly well-sorted sand, but also contains some gravel and silt-clay lenses. Aquifer thickness is generally about 18 m but, may be over 30 m in places (Reeder, 1972). It was deposited by meandering debris-laden streams flowing from the disintegrating margin of the Des Moines glacial lobe sometime between 14,000 and 12,000 years BP (Wright, 1972). After the outwash sands were deposited, stagnant ice blocks within the aquifer melted, forming the abundant lakes and wetland depressions common throughout the area (Goldstein, 1985).

Recharge to the aquifer occurs over much of its area from snowmelt and rainfall and was estimated at 17.7 cm yr^{-1} on the basis of a steady-state ground-water model developed for the aquifer (Cowdery, 1997; Puckett et al., 1999). Ground-water flow is generally from the higher elevations of the moraines on the west, north, and east sides of the aquifer toward the Otter Tail River-chain of lakes in the center of the aquifer. Wetlands, lakes and streams are in hydraulic connection with the ground water. Water loss from the aquifer is through discharge to the Otter Tail River, lakes, wetlands, pumping from wells, and through evapotranspiration.

Climate of the West Central Minnesota climate division has been described as sub-humid continental and annual average temperature and precipitation in the area during the 30-year period from 1961 to 1990 was 5.6° C and 68 cm, respectively (Stoner et al., 1993). Open water evaporation in the study area exceeds precipitation by about 10 cm yr^{-1} (Winter and Woo, 1990). Historically, the portion of the area up gradient of the study transect was prairie, surrounded by hardwood and conifer forests on the morainal uplands: however, at the time of the study, approximately 73 percent of the land was cropland.

Fertilizer nitrogen use for agricultural purposes in Otter Tail County (Figure 3a) increased from about 28 metric tons in 1945 to about 13000 metric tons in 1994 (Jerald Fletcher, 1996, West Virginia University, written communication). A major step change

in the application rate occurred about 1967 and the rate of increase has been virtually linear since about 1970 (Figure 3b). More than half of the total amount of nitrogen used during the 1945-1994 period has been applied since 1982.

Samples for this study were collected at a point on the Otter Tail River (Figure 1, 4a) at an elevation of about 407 m. Here the river is about 48 m wide, 1 m deep, and is bordered to the north by a 40-m wide wetland and a 46-m wide forest buffer zone. The forest buffer zone comprises various oak, ash, and poplar species (*Quercus, Fraxinus,* and *Populus*) with scattered spruce and fir (*Picea* and *Abies*). Vegetation in the wetland is dominated by common reed (*Phragmites australis* [Cav.] Tin. Ex Steudel), cattail (*Typha latifolia* L.), wild rice (*Zizania aquatica* L.), jewellweed (*Impatiens capensis* Meerb.), cyperus (*Cyperus strigosus* L.), orchardgrass (*Dactylis glomerata* L.), and scattered grasses and sedges. The wetland soil consists of a layer of peat up to 2 m thick, underlain by sand and gravel deposits of the aquifer. Springs and seeps in the forest and wetland suggest the presence of a ground-water discharge zone.

3. Materials and methods

3.1 Water-sample Collection and Analysis

Otter Tail River samples were collected approximately monthly at a gaging station about 1 km downstream of the intersection of the study transect and the river (Figure 1). Additional stream samples were collected and flow was measured at 1-2 upstream sites shown in Figure 1 during February 1994, June 1994, August 1994, and August 1995, to test for changes in discharge and chemistry that may have occurred as a result of ground-water discharge to the intervening 8.3 km reach. Samples were collected in multiple vertical sections using a depth-integrating sampler (Tornes, et al., 1997). Water levels at the gaging station were recorded hourly and converted to discharge with a calibrated rating curve, and individual flow measurements elsewhere were made with a current meter (Buchanan and Somers, 1969). Total nitrogen (calculated as the sum of total Kjeldahl nitrogen, nitrate, and nitrite) fluxes were calculated using the minimum variance unbiased estimator method (Cohn et al., 1989; Tornes et al., 1997).

Ground-water samples were collected from the aquifer at site OF1 (Figures 1, 4) at the terminus of the upland transect described by Puckett and Cowdery (2002). Site OF1 consisted of a nest of 5 permanent piezometers, installed at depths ranging between 3 and 13.5 m below land surface, and made of 5-cm inside-diameter, polyvinyl chloride (PVC) pipe with slotted PVC screens 0.76 meters (m) long; the exceptions being the shallowest and deepest piezometers at this location, which were 1.5 m long.

Ground-water samples were also collected along a transect that extended from piezometer nest OF1 through the wetland and into the Otter Tail River at sites A1-A5 (Figure 4) using mini-piezometers (Winter et al., 1988). Mini-piezometers were constructed of a 0.6-cm diameter, 2-m long stainless steel tube having a 2.54-cm long

screen and 2.0-cm diameter tip, nested in a 2.0-cm diameter stainless steel sleeve. The mini-piezometer was inserted into the sediment to the desired depth, and the outer sleeve was pulled back to expose the screened interval during sampling. Initially, during preliminary sampling and site selection in June 1994, mini-piezometer samples were collected at approximately 6-m intervals. In later sampling, however, this interval was increased to about 12 m, after it was determined that the differences in chemistry between intermediate sites were not of sufficient magnitude to justify continued sampling. Similarly, samples were initially collected at depths just below the bottom of the peat and again at 0.5 m below it. After it was determined that there were only minor chemical differences, the shallow samples were eliminated. Samples were collected from the mini-piezometers in August 1994, 1995, and 1997. Sampling was conducted in August because it is a period of stable, low stream flow when ground water would be most likely to contribute to surface-water quality and flow, and temperatures would be less likely to limit microbial activity. Locations and elevations of all sample sites were surveyed relative to the permanent piezometer nest (OF1) in the forest buffer zone to allow resampling at the same locations. Ground-water heads were measured relative to surface water using a portable manometer (Winter et al., 1988) and were referenced to the permanent piezometer nest elevation, which was established by surveying to the nearest USGS benchmark.

A peristaltic pump and copper tubing with a short piece of Tygon or Viton tubing in the pumphead was used to sample mini-piezometers. Permanent piezometers were sampled using a stainless steel positive displacement pump with Teflon tubing; copper tubing was used for CFC and dissolved gas sampling and the Tygon or Viton tubing was pre-tested for CFC contamination. Water temperature, specific conductance, and dissolved-oxygen (O_2) concentration were monitored continuously prior to sample collection. When these measures stabilized, sample collection began. Samples for chemical analyses were filtered through a 0.45 μm nitrocellulose filter (a silver filter was used for dissolved organic carbon (DOC) samples). Mercuric chloride preservative was added to nutrient samples during 1994 but afterward, no preservative was added and nutrient and DOC samples were shipped on ice the same day that they were collected to the U.S. Geological Survey National Water Quality Laboratory in Denver, Colorado for immediate analyses. Cation samples were preserved with nitric acid, major cations and silica were analyzed by inductively-coupled plasma spectroscopy, anions by ion chromatography, and nutrients by colorometric methods (Fishman and Friedman, 1989; Fishman, 1993; Wershaw et al., 1987). Alkalinity was determined in the field by incremental titration of filtered samples (Koterba et al., 1995). Equipment blank samples, field blank samples, replicate samples, and spiked samples showed a general lack of sampling contamination (Koterba et al., 1995; Menheer and Brigham, 1997). Sulfide (S^{2-}) was measured for most ground-water samples by the methylene blue method (Standard Methods, 1975). Samples were processed immediately using a HACH 2000 portable spectrophotometer with detection limits of 0.28 μmol L^{-1} S^{2-}. The geochemical model WATEQ as implemented in NETPATH (Plummer et al., 1994) was used for speciation and calculation of saturation indices.

To gain a better understanding of the spatial distribution of NO_3^- and potential reducing

conditions in the riparian buffer zone, in August 1994 and 1995 samples were collected from 30-40 separate locations within a 40-m wide by 140-m long segment of the study area paralleling the Otter Tail River (Figure 4a). At each location, land-surface elevation was surveyed relative to site OF1 and ground-water head, O_2, and NO_3^- were measured at a depth of about 1 m below land surface, depending on the thickness of the peat. For these samples, NO_3^- was measured in the field by the cadmium reduction method (Standard Methods, 1975) with a HACH 2000 portable spectrophotometer having detection limits of 6.4 μmol L^{-1} NO_3^-. The SigmaPlot program (SPSS, 1997) was used to produce contour plots of land-surface elevation, ground-water heads, O_2, and NO_3^-.

Dissolved gases (N_2, Ar, CO_2, CH_4, O_2) were analyzed in ground-water samples by gas chromatography after extraction in headspaces of glass samplers (Busenberg et al., 1998). Results were corrected for solubility in sample water at laboratory temperatures and have an error of $\pm$2-4 percent. Concentrations of N_2 and Ar gases dissolved in water were used to estimate the amount of nitrogen resulting from denitrification (Vogel et al., 1981; Wilson et al., 1990; Bohlke and Denver, 1995; Blicher-Mathiesen et al., 1998). This approach required the assumption that the atmosphere and denitrification were the only sources of N_2 in ground water. However, excess air can also become trapped in recharging ground water and can affect dissolved gas concentrations. Where excess air alone affects dissolved gas concentrations, N_2 and Ar increase linearly, making it possible to estimate the amount, which typically is negligible (less than 3 cc kg^{-1}) and often ignored in studies of this nature (Bohlke and Denver, 1995; Plummer and Busenburg, 1999). However, we made corrections to the excess N_2 estimates by subtracting the air-saturated water plus excess air concentrations from the measured concentrations. We estimated the original or reconstructed concentration of NO_3^- (prior to denitrification) as the sum of measured NO_3^- and excess N_2. We also applied the methods presented by Blicher-Mathiesen et al. (1998) to evaluate the potential for degassing of ground water. This method involves comparing the total partial pressures of dissolved gases in each sample to the hydrostatic pressure of the ground water at the sample depth. Where partial pressures exceed hydrostatic pressure, the potential exists for degassing.

Samples for analyses of the chlorofluorocarbons $CFCl_3$ (CFC-11), CF_2Cl_2 (CFC-12), and $C_2F_3Cl_3$ (CFC-113) were collected for age dating ground water using a stainless steel sampling apparatus under an ultra-pure nitrogen atmosphere and were flame sealed in 62 cc borosilicate glass ampoules, thus preventing atmospheric contamination (Busenberg and Plummer, 1992). Five ampoules were collected at each site, three of which were used for analyses by electron-capture gas chromatography with a detection limit of 0.3 picograms per kilogram of water (pg kg^{-1}) for CFC-11 and CFC-12 and 1.0 pg kg^{-1} for CFC-113 (Busenberg and Plummer, 1992). CFC's are known to exhibit varying degrees of susceptibility to biodegradation and sorption on organic matter, with CFC12 being least affected and CFC11 and CFC113 being the most affected (Cook et al., 1995; Lovely and Woodward, 1992; Plummer and Busenberg, 1999). Consequently, CFC12 was used in most cases for age determinations. Sample ages were assigned on the basis of comparison of CFC equilibrium partial pressures, corrected for recharge

temperature, with a chronology of atmospheric partial pressures (Busenberg and Plummer, 1992). Recharge temperatures were estimated in two ways: (1) using Ar concentrations and assuming equilibrium with the atmosphere, and (2) where Ar was not measured, on the basis of the average annual temperature (Busenberg and Plummer, 1992). Another potential source of uncertainty arises from the fact that CFC-apparent ages reflect the year in which ground water was last in contact with unsaturated zone air, but not necessarily the year in which it fell (Cook and Solomon, 1997). Previous modeling work at this site has shown that it can take from 0.5 to 1 year for water to percolate through the vadose zone to the water table, so any error would be negligible. These methods result in a potential uncertainty of about $\pm 2°$ C, which translates to an age uncertainty of about 1 year prior to 1970, 1-3 years for 1970-1990, and 3 years or more for waters that recharged after 1990. The increasing uncertainty in recent years results from the flattening of the CFC input function due to reductions in CFC usage. Because they typically require some degree of subjective interpretation, CFC age dates are referred to as model or apparent ages (Plummer and Busenberg, 1999).

3.2 Denitrification

Sediment samples were collected in August 1995 for denitrification rate assays using the acetylene block method, which blocks the conversion of N_2O to N_2 (Yoshinari and Knowles, 1976; Yoshinari et al., 1977) so N_2O production can be used to measure potential denitrification rates (Klemedtsson et al., 1988; Morris et al., 1988; Fujikawa and Hendry, 1991; Bradley et al., 1995). Sample sites were selected on the basis of water-quality data collected during the 1994 sampling and on field data from the August 1995 NO_3^- spatial distribution study. Our hypothesis was that denitrification was carbon limited in the forest at site OF1 and the wetland edge at site A1, but not under the river at site A5. Accordingly, sediment samples were collected in the forested area near the permanent piezometer nest OF1, the wetland edge at site A1, and the bottom of the river at site A5. The sediment near site OF1 was collected from the bottom of a one-meter deep, 5-cm diameter auger hole, at the water table. Sediment from the wetland edge at site A1 was collected from a 5-cm diameter, 30-cm deep auger hole, immediately below the peat layer at site A1. River sediment was collected at a depth of about 30 cm below the bed at site A5. Samples were placed in an autoclaved large-mouth glass jar, covered with water from the sample location, shipped to the laboratory on ice, and maintained at 4° C until the incubation began.

Sediments were drained to decrease background concentrations of NO_3^- and dissolved C. Known amounts of NO_3^- and C were then added to the sediments. Methodology followed that previously described by Pfenning and McMahon (1996) with the exception of the NO_3^- and C concentrations, and had a detection limit of 2 nmol L^{-1} N_2O with a prescision of $\pm 5\%$. These sediments were incubated in solutions containing 375, 714, or 1,785 μmol L^{-1} NO_3^- with no additional C to test whether denitrification was limited by NO_3^- alone, or 0, 125, or 375 μmol L^{-1} C with 375 μmol L^{-1} NO_3^- added to test whether denitrification was being limited by C. These concentrations are typical for groundwater

in the area (Puckett et al., 1999; Puckett and Cowdery, 2002).

When the experiments were completed, sediments were oven-dried and weighed and a separate aliquot of each sample was analyzed for total carbon (C) and nitrogen, using a Carlo Erba elemental analyzer. A duplicate sample was exposed to hydrochloric acid fumes to remove inorganic C, after which organic C content was measured, and inorganic C was calculated as the difference between total and organic C (Hedges and Stern, 1984). Concentrations were normalized using sediment dry weights.

N_2O production was analyzed by linear regression of the time-series data using a nonparametric, multi-factor rank-transformation test (Helsel and Hirsch, 1992) to test for significant differences ($\alpha=0.05$) in N_2O production rates among sites, and treatments. This procedure was carried out by ranking the N_2O production rates and performing an analysis of variance (ANOVA) on the ranks. This method approximates a non-parametric ANOVA on medians and is more robust than ANOVA on data not normally distributed or simply log-transformed. Where significant differences were determined, Tukey's HSD multiple comparison test was used to determine significant differences among the sites (Helsel and Hirsch, 1992).

4. Results

4.1 Surface Water

4.1.1 Hydrology

Mean daily flow during October 1, 1993-September 30, 1994 was 5.0 m^3 s^{-1} and ranged from 2.3 to 18.4 m^3 s^{-1}. Typically, flows were largest during the spring quarter (April-June) as a result of snowmelt and runoff, and during the fall quarter (October-December) following leaf fall. Flows were lowest in the winter quarter (January-March) and during the summer (July-September), with the exception of August 1993, which coincided with an unusually wet summer throughout the region (Tornes et al., 1997).

Comparisons of flow at 2-3 points on the river during February 1994, June 1994, August 1994 and August 1995 (Table 1) revealed that flow increased through the 8.3 km study reach by as much as 20 percent during February 1994 and by 14 percent during late August 1994. It is interesting to note that the August 1994 increase of 0.4 m^3 s^{-1} was almost as great as the 0.42 m^3 s^{-1} value recorded in February 1994. The August sampling was on the last day of the month at the end of the growing season, when evapotranspiration losses may have been greatly reduced. The increases in flow during what were typically low-flow periods are what would be expected for a river that gains flow from ground–water discharge. Therefore it would appear that average ground-

water discharge within the 8.3 km long reach is about 0.4 m^3 s^{-1}. Flow through the same reach was constant in June 1994 but decreased by 9.2 percent (0.2 m^3 s^{-1}) in early August 1995. Assuming that the ground-water contribution of 0.4 m^3 s^{-1} is relatively constant, this suggests a net loss of about 0.4 m^3 s^{-1} in June 1994 and 0.6 m^3 s^{-1} in August 1995.

4.1.2 Water Chemistry

Nutrient concentrations in the river (Table 2) were small in spite of the intense agricultural inputs in fertilizer reported by Puckett et al. (1999). Concentrations of NO_3^- were small and in a third of samples were below the reporting limit (3.6 μmol L^{-1}). The largest concentrations of NO_3^- and NH_4^+ typically occurred during the winter months, when biological uptake would have been lowest, whereas the concentrations were smallest during the summer, when biological uptake would have been most intense. Comparisons of NO_3^- and Cl^- concentrations at 3 points on the river during August 1994 and August 1995 revealed that concentrations of both constituents typically increased through the study reach (Table 1). On both sampling dates, concentrations of NO_3^- increased only in the lower segment of the reach whereas concentrations of Cl^- increased throughout the entire reach, indicating that evaporation alone was not responsible for the increase in concentration and that ground-water discharges were contributing NO_3^- and Cl^- to the stream.

Most nitrogen in the river was present in the organic form; typically about 86 percent of nitrogen was organic. Furthermore, about 77 percent of total organic nitrogen (TKN) was in a dissolved form (DKN). Concentrations of all forms of organic nitrogen were smallest during the growing season and largest in the winter months, probably due to decomposition of plant matter from the previous growing season. Total nitrogen fluxes were 127.5 Mg N in 1994. The largest fluxes of total nitrogen occurred during the spring (40.1 Mg N) and fall (39.9 Mg N) high-flow quarters with about 31 percent being transported in each. The winter (27.9 Mg N) and summer (19.7 Mg N) quarters accounted for about 22 and 16 percent of the annual flux, respectively.

Like many rivers in western Minnesota, Otter Tail River chemistry (Table 2) is dominated by Ca^{2+}, Mg^{2+}, and HCO_3^- (Tornes et al., 1997). Glacial deposits in the area have been shown to contain calcite and dolomite, which controls the evolution of water chemistry (Berndt, 1987; Puckett and Cowdery, 2002; Tucillo et al., 1999). As a consequence, pH and concentrations of Ca^{2+}, Mg^{2+}, and HCO_3^- are about what would be expected for waters near equilibrium with calcite and dolomite, and saturation indices calculated in WATEQ were 0.3 and 0.4, respectively. Concentrations of Na^+ and K^+ on the other hand were small, accounting for less than 6 percent of total cations on an equivalent basis, and Cl^-, SO_4^{2+} and SiO_2 concentrations were similarly small. There was virtually no difference between dissolved phosphorus and orthophosphate

indicating that orthophosphate was the dominant dissolved form; however, their concentrations were small relative to total phosphorus, indicating that most phosphorus probably was associated with organic matter or suspended sediment. Dissolved Fe^{2+} and Mn^{2+} were minor constituents, which is to be expected in waters that are typically well oxygenated. Dissolved organic carbon (DOC) concentrations were large, probably as a result of the wetlands along the river and in the lakes through which it flows.

4.2 Ground Water

4.2.1 Hydrology

Water levels in the permanent piezometers OF1S, OF1A, OF1B, and OF1C were all consistently within a few centimeters of each other (medians were 407.54 m in August 1995 and 407.75 m in August 1997). Water levels in the deepest piezometer (OF1D) however were as much as 1.9 m greater than the other piezometers at the site (408.65 m in August 1995 and 409.66 m in August 1997), probably as a result of a thin silt layer immediately above it, indicating a strong upward flow potential in the deepest part of the aquifer adjacent to the river.

Observations made along the riparian wetland study transect (A1-A5) revealed ground-water seepage in the vicinity of site A2, and mini-piezometer head measurements were as much as 50 cm higher relative to surface water, decreasing towards the river (Figure 4b,c). Ground-water heads at other sites throughout the wetland (Figure 4b,c) were variable and ranged as much as 50 cm higher relative to surface water in one area near the river. There were also seepage areas at various locations along the wetland edge and springs were noted in the forested buffer zone. In general, these results indicate an area of potential ground-water discharge along the axis of the transect and across the wetland extending out under the river.

Given reported hydraulic conductivities for the aquifer materials of 30.5-73.2 m day^{-1}, average porosity of 0.25-0.3 (Cowdery, 1997; Puckett and Cowdery, 2002), and the measured heads and water levels, it is possible to estimate the average velocity of pore waters beneath the wetland. Gradients between piezometers OF1 and A4 ranged from 0.0042-0.026 resulting in estimated average velocities of 0.4-7.6 m day^{-1}. At these velocities and assuming horizontal flow, it would take from 7-128 days with a median of 29 days, for water flowing under the wetland to traverse the 55.2 m from the permanent piezometer nest at OF1 to the outer edge of the wetland at A4.

4.2.2 Dissolved Gases

With the exception of site OF1S, O_2 concentrations (Tables 3, 4) decreased with increasing age, depth, and distance along the wetland transect, suggesting that oxygen was being consumed within the system, presumably to oxidize organic carbon. Waters older than about 8 years, although not completely anoxic, were extremely hypoxic

($O_2 < 16$ μmol L^{-1}).

Concentrations of N_2 (Table 4, Figure 5) ranged from near equilibrium with the atmosphere (682 μmol L^{-1} at 5.6° C) to 958 μmol L^{-1} with a median of 842 μmol L^{-1}. Ar concentrations ranged from 15.0 to 18.9 μmol L^{-1}. Excess air estimates ranged from 0.6 to 1.41 cc kg^{-1} with a median of 1.06 cc kg^{-1}. Concentrations of both N_2 and excess N_2 were lower in OF1S and A1, then increased with depth and distance along the transect before decreasing again. Excess N_2 concentrations were as large as 284 μmol L^{-1}, equivalent to 568 μmol L^{-1} NO_3^- assuming the excess N_2 was derived from denitrification.

Sulfide (Table 4) was only detected in ground water from sites that also had relatively small SO_4^{2-} concentrations, indicating that SO_4^{2-} reduction was occurring there. Because of the relatively large concentrations of Fe^{2+} and limited availability of SO_4^{2-} (Table 3) it is unlikely that free S^{2-} would reach even moderate concentrations due to its tendency to form metal sulfide precipitates.

Concentrations of CH_4 were negligible except in the deepest two piezometers at OF1 and towards the end of the wetland transect, with the largest concentrations at OF1D and A5 (Table 3). The large concentrations at A5 indicate strong reducing conditions. Concentrations of CH_4 were so large at this site that we believe bubbles of gas formed, creating a space into which other gases evolved. Evidence of degassing can be seen in the low concentrations of N_2 and Ar relative to other sample sites and the fact that both N_2 and Ar concentrations are much less than their equilibrium concentrations. In addition, the sum of gas partial pressures equaled or exceeded hydrostatic pressure at site A5, indicating that degassing is likely to have occurred.

4.2.3 CFC age dates

CFC apparent ages ranged from 8 to 50 years (Table 4), displayed a pattern of increasing age with increasing depth at site OF1, and reflect the travel times from the upland recharge areas and the vertical age distribution of ground water in the up-gradient aquifer (Stoner et al., 1997; Puckett and Cowdery, 2002). Apparent ages also increased from 8 to 45 years with increasing distance along the study transect from site A1 through A4. Because of degassing, age dating at site A5 was impossible.

It is important to note that the 37-year difference in apparent ages between OF1S and A4 is inconsistent with the 7-128 day travel times estimated earlier for ground water to travel the distance from OF1S to A4. In order for the assumption of horizontal flow to be correct, there should be no significant difference in water ages across the riparian wetland transect. In fact, the age distribution along the wetland transect was a horizontal reflection of the vertical age distribution at OF1, suggesting that ground water of progressively greater age from the up-gradient aquifer was discharging below the wetland and was the reason for the horizontal age distribution.

4.2.4 Water Chemistry

Ca^{2+}, Mg^{2+}, and HCO_3^- were the dominant dissolved species, which is consistent with what is known of the outwash mineralogy and agricultural applications. Puckett and Cowdery (2002) found that ground-water carbonate chemistry was controlled by dissolution of $CaCO_3$ and $CaMg(CO_3)_2$. Interestingly, the concentrations of Ca^{2+} and HCO_3^- were considerably larger in ground water than in the river but Mg^{2+} concentrations were about the same, suggesting that as ground water discharges into the river $CaCO_3$ may precipitate. This is further supported by the fact that ground water generally was under saturated with $CaCO_3$ and $CaMg(CO_3)_2$ whereas the river was slightly over saturated with both.

SiO_2 concentrations were consistently larger in ground water than in the river and accumulate as a product of silicate mineral weathering. Chloride concentrations also were larger in ground water than in the river but tended to decrease with increasing depth and distance along the transect. Chloride occurs in fertilizer as potassium chloride (KCl) and is a common contaminant associated with agricultural areas (Anderson, 1993). Comparisons of Cl^- and SiO_2 concentrations in Otter Tail River water and in the ground waters sampled under the wetland and in the adjacent up-gradient aquifer (Figure 6) indicate that mixing of ground and surface waters in the riparian zone is unlikely since the wetland samples did not fall along the mixing line between the two end members. Although concentrations of both Cl^- and SiO_2 were significantly larger in wetland and upland ground water than in the river, they did not differ significantly ($\alpha=0.05$) among themselves.

SO_4^{2-} concentrations in ground water were much larger than in the river but tended to decrease with increasing depth at OF1 and distance along the transect from the forest to the river. There is little available sulfur in the outwash sediments; therefore, it is commonly supplied as an agricultural supplement either as gypsum ($CaSO_4 \cdot 2H_2O$) or in more recent years as ammonium sulfate ($(NH_4)_2SO_4$) at rates of 28-336 kg S ha^{-1} (Denzel Cooper, University of Minnesota Extension Service, oral communication, 1996). Puckett and Cowdery (2002) estimated these application rates would result in a spatially average concentration of 495-5930 µmol SO_4^{2-} L^{-1} and therefore can easily account for the observed ground-water concentrations. The lower concentrations are associated with the oldest ground waters, which is to be expected because less fertilizer was used at that time. Also, the older waters are more likely to have undergone some degree of SO_4^{2-} reduction; a conclusion supported by the observation that S^{2-} concentrations increased sharply in those samples in which SO_4^{2-} concentrations sharply decreased.

Manganese concentrations reached as much as 11 µmol L^{-1} and typically reached a maximum where most NO_3^- had been consumed and Fe^{2+} was increasing. Iron concentrations displayed a large range, from below detection to as high as 131 µmol L^{-1}. Such relatively large concentrations of dissolved iron suggests that the predominant terminal electron accepting process had changed from reduction of O_2, NO_3^-, and manganese oxides to iron oxide reduction. This pattern agrees with the

reported redox sequence in which manganese oxide reduction occurs at $p\varepsilon$ levels after denitrification and before iron oxide reduction (Stumm and Morgan, 1981).

Concentrations of NO_3^- behaved like O_2, generally decreasing with increasing age, depth, and distance along the transect (Tables 3, 4). This decreasing pattern suggests that once O_2 was limiting, NO_3^- was utilized as the terminal electron acceptor in the oxidation of organic carbon. Samples greater than about 30 years old were virtually depleted of NO_3^-. NH_4^+ concentrations generally increased with increasing age, depth, and distance along the transect (Table 3). Although the exact source of NH_4^+ was not determined, in other studies of sediments in similar redox environments, NH_4^+ production has been traced to mineralization of nitrogen in buried organic matter and not to dissimilatory nitrate reduction (McMahon et al., 1999). Other forms of nitrogen were negligible. Excess N_2 concentrations first increased and then decreased with both increasing age and depth at OF1 and increasing age and distance along the transect from A1 to A4 (Table 4). The decrease in measured NO_3^- concentrations was related primarily to removal of NO_3^- by denitrification as well as lower fertilizer use in earlier years. The more complex pattern for excess N_2 occurred because in younger ground water, as NO_3^- was being converted to N_2 through denitrification, its concentration increased. The decrease in excess N_2 concentrations in samples of older ground water, however, reflected the smaller amounts of fertilizer used in the earlier years so there was less NO_3^- to convert to N_2. The distribution of the reconstructed NO_3^- concentrations calculated as the sum of measured NO_3^- and excess N_2 was similar to that of measured NO_3^-. The decrease in reconstructed NO_3^- concentrations with both increasing age and depth was due to the fact that less fertilizer was applied in the earlier years when these older ground waters recharged. About 69% (adjusted $r^2=0.689$) of the variance in reconstructed NO_3^- concentrations was explained by the corresponding ground-water age with the remaining variation presumably due to annual variability in the amount of fertilizer applied in the past, the amount of nitrogen removed in harvested crops, volatilization and other losses prior to and during recharge.

Results of the spatial distribution study revealed overlapping areas of relatively high O_2 and NO_3^- concentrations (Figure 7a, b) that appear to be associated with ground–water highs between elevations of 407.4 and 407.55 meters (Figure 4b, c). Examination of the heads also suggests that like the study transect (A1-A5) the generalized discharge zone actually intersects the river at an angle of about 45 degrees instead of being perpendicular to it. The result is that although O_2 and NO_3^- concentrations decreased towards the river, NO_3^- concentrations still exceeded 400 μmol L^{-1} about 70 m upstream of site A3 at the edge of the river and were greater than 200 μmol L^{-1} under the river.

The presence of NO_3^- at relatively large concentrations under the river is significant in that it indicates that ground water containing NO_3^- was able to move along flow paths, under the wetland, where little if any NO_3^- was removed. Furthermore, the spatial distribution study results demonstrate the potential heterogeneity of the riparian zone and the need to conduct these types of riparian zone studies. For example, on the basis of results of the wetland transect portion of the study from OF1 to A5 alone, it would be easy to incorrectly infer that all NO_3^- was removed before it reached the river. However,

our results from the spatial distribution study clearly show that at some locations, NO_3^- does reach the river and explains how the downstream increase in NO_3^- observed in the Otter Tail River occurred.

4.3 Denitrification

Denitrification rates (expressed as μmol N_2O g^{-1} d^{-1}) measured by the acetylene block incubation method generally increased with increasing organic C concentrations, especially in sediments from OF1 and A1 (Figure 8a). Site A5 sediment incubation responses (Figure 8a) were virtually the same for the 125 and 375 μmol L^{-1} organic C amendments, indicating that organic C did not limit denitrification beneath the river. Statistically, the responses to NO_3^- additions of 375 and 714 μmol L^{-1} with C amendments held constant, were not significantly different from one another, but were significantly less than the rates at 1785 μmol L^{-1}. In spite of the significantly larger rates at 1785 μmol L^{-1} NO_3^-, the slopes of regression lines fit through the rates for each site were all zero, indicating the response to NO_3^- addition alone was not significant (Figure 8b).

The strongest denitrification response therefore was to organic C amendment, particularly the highly linear response of forest (OF1) and wetland edge (A1) sediments (Figure 8a). This positive response to organic C and limited response to NO_3^- indicates that denitrification is organic C limited at all sites except in river sediments at A5. The wetland edge sediments at A1, with their moderate organic C content and relatively high ground-water NO_3^- concentration (Table 5), had the lowest overall denitrification rates in the absence of added organic carbon, but these rates were equal to or greater than rates for the forest sediments at OF1 when both organic C and NO_3^- were added (Figures 8a, b).

5. Discussion

Several studies have reported denitrification rates for sand and gravel sediments (Trudell et al., 1986; Smith and Duff, 1988; Lowrance, 1992; Smith et al., 1996; Aelion and Shaw, 2000; Tesoriero et al., 2000). These rates fall within a range of 0-0.44 μmol N_2O g^{-1} day^{-1} however those reported by Smith and Duff (1988), Smith et al. (1996), and Lowrance (1992) were at the lower end of that range (0.001-0.007 μmol N_2O g^{-1} day^{-1}) for aquifers in Cape Cod and south Georgia, respectively. Trudell et al. (1986), Aelion and Shaw (2000), and Tesoriero et al. (2000) covered the entire range of values (0-0.44 μmol N_2O g^{-1} day^{-1}) for aquifers and stream sediments in southern Ontario, South Carolina and, western British Columbia, respectively. The Otter Tail results (0.012 to 0.417 μmol N_2O g^{-1} day^{-1}) are similar to those reported by the latter group of investigators and the aquifer is similar in composition and organic carbon content to the southern Ontario site, and denitrification was carbon limited in both studies.

Where the oxidation of organic carbon does occur, O_2 is thermodynamically favored over NO_3^- as the terminal electron acceptor (Stumm and Morgan, 1981; Korom, 1992; Chapelle, 1993; Chapelle et al., 1995). When sufficient O_2 is consumed to limit microbial aerobic respiration, denitrification becomes the thermodynamically favored terminal electron accepting process, leading to lower NO_3^- concentrations as well. Once most of the available NO_3^- is consumed, bacteria utilize manganese oxides and then iron oxides as terminal electron acceptors. Under very strong reducing conditions, bacteria capable of deriving energy from sulfate reduction and methanogenesis are favored. The net result of this evolution of water chemistry is a predictable sequence in which O_2 and then NO_3^- are consumed, manganese and iron come into solution, sulfate is consumed and sulfide may come into solution, and finally methane may appear in solution (Stumm and Morgan, 1981; Korom, 1992; Chapelle, 1993; Chapelle et al., 1995). By sampling along ground-water flow paths, it may be possible to observe this sequence and thereby infer the redox state and dominant chemical processes involved.

The distribution of the redox sensitive constituents measured in this study suggest that as ground water flows under the wetland peat it passes first through a zone between sites OF1 and A1 where O_2 was being reduced and the presence of about 30-60 μmol L^{-1} excess N_2 indicated limited denitrification was occurring (Tables 3, 4), then between A1 and A2" where NO_3^- was completely denitrified to N_2 gas (Figure 9a). Between sites A2" and A3, Fe^{2+} came into solution (Figure 9a) presumably as a result of iron oxide reduction, and between sites A3 and A5 there was almost complete reduction of SO_4^{2-} to S^{2-} (Figure 9b). Also between sites A3 and A5 CH_4 was produced as the result of methanogensis (Figure 9b). The resulting redox sequence (Figure 9c) is similar to that conceptualized by Correll et al. (1992) for horizontal flow systems of the Atlantic Coastal Plain and therefore appears to support our hypothesis that NO_3^- was being removed in the riparian buffer zone by denitrification due to the progressively stronger redox conditions under the wetland. This interpretation would assume that ground water was flowing horizontally beneath the wetland in a manner similar to that shown in Figure 2a.

Horizontal flow systems like that depicted in Figure 2a have been shown to occur in a number of studies of denitrification in riparian zones. Mengis et al. (1999) demonstrated denitrification in a southern Ontario riparian zone having saturated thickness of <1.5 m and a horizontal flow system over a clay till. Results of a study by Devito et al. (2000) demonstrated denitrification along horizontal flow paths in another riparian zone in southern Ontario having 4-6 m saturated thickness above a clay confining layer. Several studies in the southeastern Atlantic Coastal Plain of the United States suggest that shallow flow systems of this type may be common there (Correll et al., 1992; Jacobs and Gilliam, 1985; Jordan et al., 1993; Lowrance, 1992; Puckett, 1999; Shedlock et al., 1993). For example, Correll et al. (1992) and Jordan et al. (1993) reported most NO_3^- was removed from ground water in riparian zones in Maryland having saturated thickness of <2 m and horizontal flow above a clay confining unit. Lowrance et al., (1984) reported similar results for a site in Georgia having saturated

thickness of <1.5 m. Correll et al. (1992) proposed that the presence of shallow confining units was an important factor in the function of these riparian buffer zones in that ground water was forced to remain in contact with vegetation and reducing conditions there. Although a clay lens about 30 cm thick was identified at a depth of 10.5 m at site OF1, there are no known shallow clay confining units beneath the Otter Tail riparian zone, and the underlying clay till surface is about 16 m below land surface.

Although the results seem to support the hypothesis of horizontal flow, examination of the data from the piezometers at site OF1 (Figure 10) revealed a vertical chemical sequence similar to the horizontal sequence shown in Figure 9. Ground water in the upper portion of the aquifer at site OF1S was suboxic (<65 μmol L^{-1} O$_2$) (Tables 3, 4) and the presence of about 60 μmol L^{-1} excess N$_2$ indicates that some denitrification had taken place. At sites OF1A and OF1B, an almost total lack of O$_2$ and large amounts of excess N$_2$ indicated that this zone was dominated by denitrification. Between sites OF1B and OF1C, NO$_3^-$ was totally removed and reduction of iron oxides resulted in Fe^{2+} coming into solution (Figure 10a). Also at OF1C (Figure 10b), S^{2-} was present and SO$_4^{2-}$ concentrations decreased sharply, indicating that SO$_4^{2-}$ reduction was occurring and some CH$_4$ was present, indicating methanogensis was beginning. Finally, at OF1D, SO$_4^{2-}$ concentrations further decreased and CH$_4$ increased indicating that methanogensis was becoming the dominant redox process. The resulting redox sequence (Figure 10c) was previously described by Puckett and Cowdery (2002) for the up-gradient aquifer and results from a combination of oxidation of organic carbon in the sediments and the relatively long (>50 year) residence time. We propose that the redox sequence shown in Figure 9c is a horizontal reflection of the vertical sequence between OF1S and OF1D (Figure 10c) and supports our alternative hypothesis that the changes in chemistry along the riparian wetland transect were the result of progressively older and more chemically reduced ground water from the up-gradient aquifer discharging under the wetland in a manner similar to that shown in Figure 2b.

The similar water chemistry and redox sequences, therefore, can lead to conflicting interpretations as to which of the hydrologic flow systems are correct; however, the CFC apparent-age dates and ground-water head measurements provide the most compelling evidence of which of the flow systems is most plausible. Ground waters at site OF1 become progressively older with depth, ranging from 8 to 50 years in age (Table 4). This age distribution arises due to the differential travel times and flow-path lengths from the up gradient recharge zones to the discharge zone at the river (Stoner et al., 1997; Puckett and Cowdery, 2002). The age distribution found along the wetland transect (Table 4) indicates that ground water similar in age and chemistry to that at OF1 was discharging under the wetland and this conclusion is supported by the ground-water modeling results of Puckett and Cowdery (2002) shown in Figure 11. Head measurements along the wetland transect also provide evidence of a ground-water discharge zone there. Furthermore, the presence of a horizontal flow system is unlikely given our calculations of potential ground-water velocities, which indicated that if horizontal flow was occurring there should be no measurable differences in age along

the wetland transect.

The flow system shown in Figures 2b and 11 explains why the age distribution and water chemistry found at site OF1 would be repeated in the discharge zone associated with the wetland transect. As shown, shallow, younger ground water discharges in seeps and springs at the break in slope near the edge of the wetland, and deeper, older ground water discharges at progressively greater distances along the transect. This flow system also indicates that the presence of progressively more reduced zones along the transect are largely the result of the progressively older and more reduced ground waters from the up-gradient aquifer discharging there. Consequently, a horizontal flow system such as that shown in Figure 2a was ruled out in favor of the deeper version shown in Figure 2b.

In the absence of shallow confining units, ground-water flow systems similar to those shown in Figure 2b may develop, the depth and complexity of which are determined largely by the general slope and local relief (Toth, 1963). Bohlke and Denver (1995) demonstrated similar flow system dynamics in their investigation of two agricultural watersheds in Atlantic Coastal Plain of Maryland. In their study, flow paths up to 20 m deep exhibited residence times of 30-50 years, and bypassed the riparian zone to discharge directly into a stream. Modica et al. (1998), working in similar watersheds in New Jersey with depths up to 55 m, found residence times >45 years also and ground water discharging directly to streambeds. The results of our study indicate that saturated thickness of as little as 16 m is adequate for development of these long, deep flow systems. Depending on their configuration, these deeper flow systems may result in ground water being discharged into both the riparian zone and streambed, or directly into streambeds alone.

6. Conclusions

Moderately deep flow systems like that identified in this study pose several implications for the effectiveness of riparian buffer zones to remove NO_3^- and also for researchers investigating the processes involved. Such deep flow systems may allow NO_3^- in ground water to be carried beneath riparian buffer zones and discharge unaltered into streams. The riparian buffer zone in this study had only a minor role in preventing NO_3^- in ground water from reaching the Otter Tail River for two reasons: (1) most NO_3^- had been removed by denitrification in the up-gradient aquifer, and (2) shallow ground water containing NO_3^- was able to move along some flow paths below the riparian zone where little NO_3^- was removed. Although we did not investigate the process, it is likely that some NO_3^- was removed from discharging ground water as it moved upward through the peat and hyporheic zone of the streambed.

Such moderately deep flow systems make it necessary for investigators to develop a

complete understanding of the hydrologic flow system in the study area and the up-gradient aquifer in order to be able to distinguish between biogeochemical processes that may be taking place in the riparian buffer zone and those that are controlled instead by processes in the up-gradient aquifer. For example, by sampling along a discharge gradient across a riparian buffer zone like the one reported here, investigators may misinterpret decreases in NO_3^- concentrations occurring due to either increasing age or denitrification in the up-gradient aquifer as evidence for denitrification in the riparian buffer zone. These conclusions are especially applicable to aquifers where a shallow confining layer is absent. More importantly, by developing an understanding of the hydrology and biogeochemistry of both the riparian and up-gradient aquifer and how they interact, we can in the end develop a more accurate capability to predict when and where riparian buffer zones will be most effective in protecting water quality.

As we have shown in this study, residence time and age of ground water are important factors because fertilizer nitrogen use throughout the United States has increased 20 fold in the last 55 years. Consequently, long and deep flow systems contain older ground waters with potentially less NO_3^- simply because less fertilizer was used when these waters entered the aquifer. In addition, long residence times may allow biogeochemical processes to remove NO_3^- even in systems where the process is carbon limited. Conversely, short and shallow flow systems have short residence times allowing less time for NO_3^- to be removed by biogeochemical processes, and greater potential for larger NO_3^- concentrations because more fertilizer may have been applied at the time of recharge. These differences in flow systems pose challenges for NO_3^- management strategies. Although shallow flow systems with short flow paths and short residence times may contain the largest NO_3^- concentrations, they will respond more quickly (on the order of a few years to a couple decades) to decreased NO_3^- inputs in the recharge area. However, deep flow systems with long flow paths and long residence times may require several decades to a century for decreases in NO_3^- input to be reflected in the discharge zone. As a compensating factor, longer residence times may provide sufficient time for slow reactions, such as the carbon-limited denitrification noted at this site, to remove NO_3^- before it is discharged to surface waters.

Acknowledgments

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Table 1. Changes in discharge and chemistry at 2-3 points on the 8.3 km study reach of the Otter Tail River. [Site 1 is the furthest upstream site and Site 3 is the gage site shown in Figure 1. Discharge units are $m^3\ s^{-1}$ and NO_3^- and Cl^- are $\mu mol\ L^{-1}$. Values reported as "0" were less than the detection limit.]

Date	Site 1	Site 2	Net Change	Site 3	Net change	Total change
February 1994						
Discharge	2.1	---	---	2.5	0.4	0.4
June 1994						
Discharge	5.0	5.0	0	5.0	0	0
August 1994						
Discharge	2.6	2.8	0.2	3.0	0.2	0.4
NO_3^-	0	0	0	5.1	5.1	5.1
Cl^-	81.7	90.1	8.4	95.8	5.7	14.1
August 1995						
Discharge	2.1	2.1	0	1.9	-0.2	-0.2
NO_3^-	10	9.3	-0.7	12.1	2.8	2.1
Cl^-	87.3	90.1	2.8	98.6	8.5	11.3

Table 2. Concentrations of selected constituents in the Otter Tail River between
February 8, 1993 and August 2, 1995. [All concentrations are μmol L^{-1} with the
exception of pH which is in standard units; DKN and TKN are reported as μmol L^{-1} N, dissolved organic carbon (DOC) is reported as μmol L^{-1} C, sample depths
are in meters. DKN=Dissolved Kjeldahl Nitrogen, TKN=Total Kjeldahl Nitrogen.
Values reported as "0" were less than the detection limit.]

Constituent	Median	Range
pH	7.9	7.3-8.4
O_2	246.9	68.8-393.8
HCO_3^-	3696	3229-4802
Ca^{2+}	1048	923-1322
Mg^{2+}	863.7	740.3-1111
Na^+	200.1	156.6-282.8
K^+	56.3	30.7-76.7
SiO_2	233.0	124.8-316.2
Fe^{2+}	1.68	0.32-3.2
Mn^{2+}	0.96	0.29-2.4
Cl^-	90.3	62.1-141.1
SO_4^{2-}	27.1	10.4-44.8
PO_4^{3-}	0.2	0-1.0
DP	0.2	0-1.0
TP	1.0	0.20-1.9
NO_3^-	5.0	0-46.4
NH_4^+	2.1	0.5-15.0
DKN	35.7	28.6-57.1
TKN	46.4	28.6-64.3
DOC	675.0	566.7-1000

Table 3. Median concentrations of major-ions in samples collected between 1994 and 1997. [All concentrations are µmol L^{-1} with the exception of pH which is in standard units; organic nitrogen (Org-N) is reported as µmol L^{-1} N, dissolved organic carbon (DOC) is reported as µmol L^{-1} C, sample depths are in meters. Values reported as "0" were less than the detection limit.]

Site	Depth	pH	O$_2$	HCO$_3^-$	Ca^{2+}	Mg^{2+}	Na$^+$	K$^+$	SiO$_2$	Fe^{2+}	Mn^{2+}	Cl$^-$	SO$_4^{2-}$	PO$_4^{3-}$	NO$_3^-$	NH$_4^+$	Org-N	DOC
OF1S	3.35	7.16	9.4	5343	2495	1172	100.1	35.8	416.0	0	0.4	479.6	249.8	0.6	928.3	0.7	6.4	149.9
OF1A	5.19	7.43	43.8	4796	2196	946.0	87.0	38.4	366.1	0	0	423.2	333.1	0.6	628.4	0.6	6.5	91.6
OF1B	6.54	7.36	17.2	4605	2221	946.0	82.7	40.9	366.1	0	1.5	371.0	327.9	0.6	609.9	1.0	6.0	108.2
OF1C	9.97	7.22	2.3	5446	1946	863.7	139.2	40.9	432.6	50.7	11.3	162.2	84.3	1.3	0	20.5	4.2	199.8
OF1D	13.11	7.55	3.1	6058	1971	863.7	200.1	42.2	432.6	79.7	3.7	45.1	10.4	5.1	0	45.7	7.9	262.3
A1	1.0	7.34	101.1	4932	2495	1111	87.0	37.1	416.0	0	0	564.2	301.9	1.1	1249.6	1.8	5.3	104.1
A2	1.45	7.50	15.6	4720	2183	946.0	80.5	33.2	366.1	0	0	338.5	333.1	0.5	531.6	1.4	5.7	104.1
A2"	1.3	7.41	8.9	4739	2146	884.3	80.5	38.4	357.8	3.1	5.9	270.8	312.3	0.9	43.7	7.5	0	124.9
A3	1.0	7.31	1.8	5449	2146	884.3	84.8	42.2	549.1	55.5	7.6	310.3	244.6	1.4	0	11.1	3.2	154.3
A4	1.0	7.25	6.3	5655	2046	863.7	82.7	43.5	582.4	58.0	5.6	259.5	66.1	4.4	0	34.7	4.6	183.2
A5	0.5	7.06	10.2	6517	2171	822.6	113.1	51.1	865.3	131.2	7.5	172.1	0.5	2.7	0	194.6	27.3	283.1
River	---	7.99	246.9	3696	1048	864.0	200.1	56.3	233.0	1.68	0.9	90.3	27.1	0.2	5.0	2.1	44.3	675.0

Table 4. Median concentrations of S^{2-}, dissolved gases, NO_3^-, excess N_2 (Xs N_2), reconstructed NO_3^- (ΣNO_3^-), and CFC apparent ages of samples collected between 1994 and 1997. [All concentrations are µmol L^{-1} and ages are in years. NO_3^- concentrations may differ from Table 3 because only samples having paired N_2 gas data were included in the calculations. Values reported as "0" were less than the detection limit.]

Site	S^{2-}	O_2	CO_2	CH_4	Ar	N_2	Xs N_2	NO_3^-	ΣNO_3^-	CFC Apparent Age
OF1S	0	11.5	788.6	0.1	17.2	746.3	60.3	1071.4	1192.0	8
OF1A	0	37.5	545.5	0	16.7	880.0	215.2	628.6	1059.0	22
OF1B	0	10.0	521.9	0	17.6	928.2	217.0	610.7	991.0	24
OF1C	0.78	2.3	600.8	15.5	18.2	957.3	243.5	0	487.0	46
OF1D	0.84	4.9	621.6	214.7	18.6	859.8	114.7	0	229.4	50
A1	0	87.5	690.9	0	17.2	712.6	29.5	1000.0	1059.0	8
A2	0	12.1	518.2	0	16.9	903.9	232.5	528.6	993.6	24
A2"	0	10.4	629.0	0.3	16.3	858.3	211.3	42.9	465.5	30
A3	0	2.6	865.1	11.6	16.3	803.8	155.6	0	311.2	28
A4	1.84	1.7	801.0	23.2	16.7	738.4	32.4	0	64.8	45
A5	1.00	2.2	1416.5	1010.8	10.1	340.2	--	0	--	--

Table 5. Organic carbon and nitrogen content (in percent) of the sediments and
concentrations (μmol L^{-1}) of DOC, NO_3^-, NH_4^+, and O_2 in ground water from
each site at the time of sample collection. [Dissolved organic carbon (DOC) is
reported as μmol L^{-1} C; values reported as "0" were less than the detection
limit.]

	OF1	A1	A5
Organic carbon	0.38	0.69	1.08
Nitrogen	0.055	0.060	0.065
DOC	100.0	100.0	283.3
NO_3^-	599.8	1099.7	0
NH_4^+	1.4	1.4	150.0
O_2	15.6	101.3	1.6
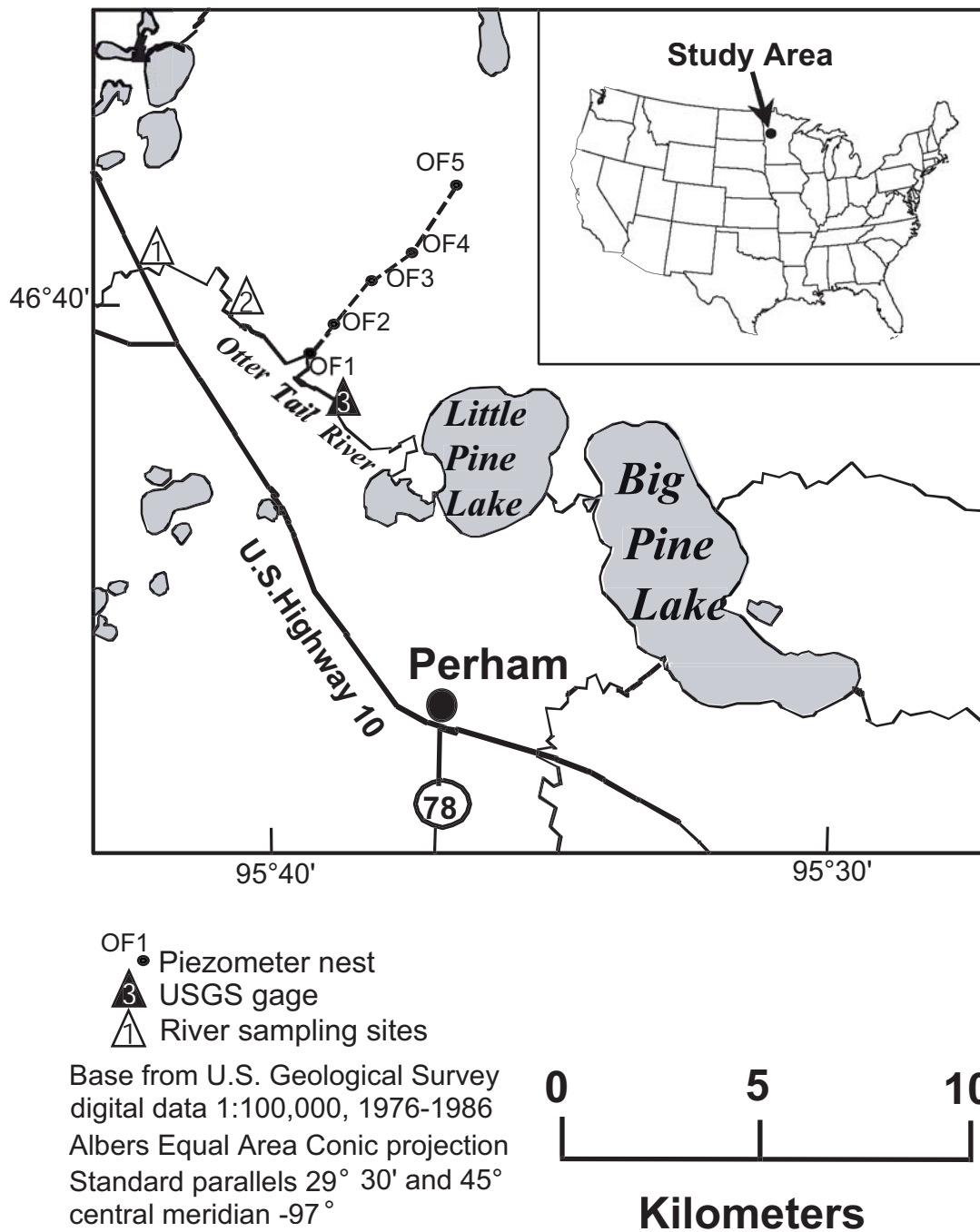
Figure 1. Location of the study area north of the Otter Tail River along with the up-gradient aquifer transect.

(a)

River

(b)

River
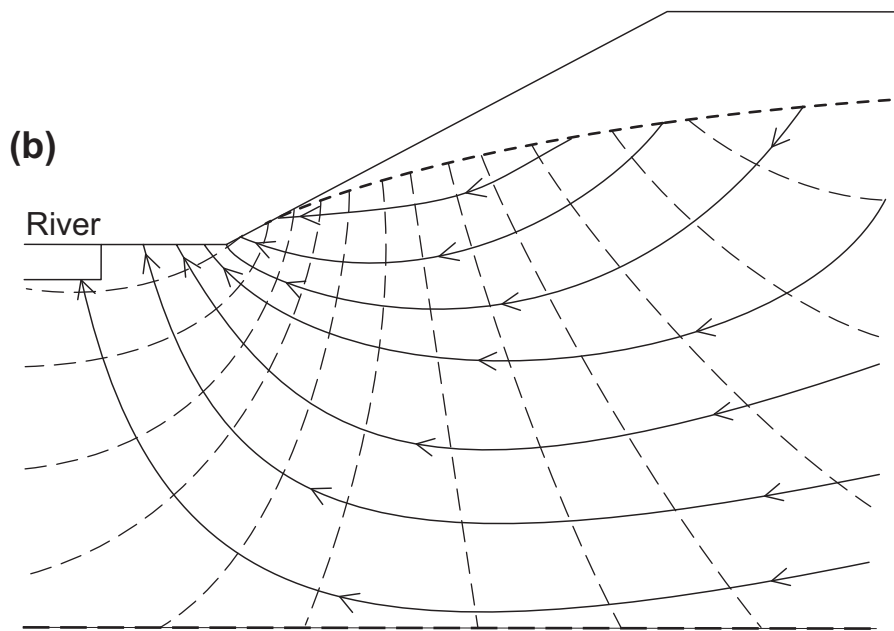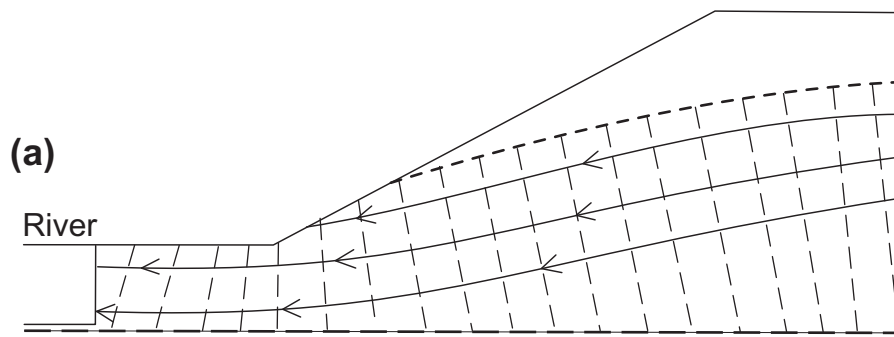
Explanation

- - - - - - - Water table

⟵──────── Direction of ground-water flow

⟜ ─ ─ ─ Line of equal hydraulic head

─ ─ ─ ─ Confining unit

Figure 2. Conceptual flow systems showing (a) shallow horizontal and (b) deep parabolic
flow paths (after Patton and Hendron, 1974).
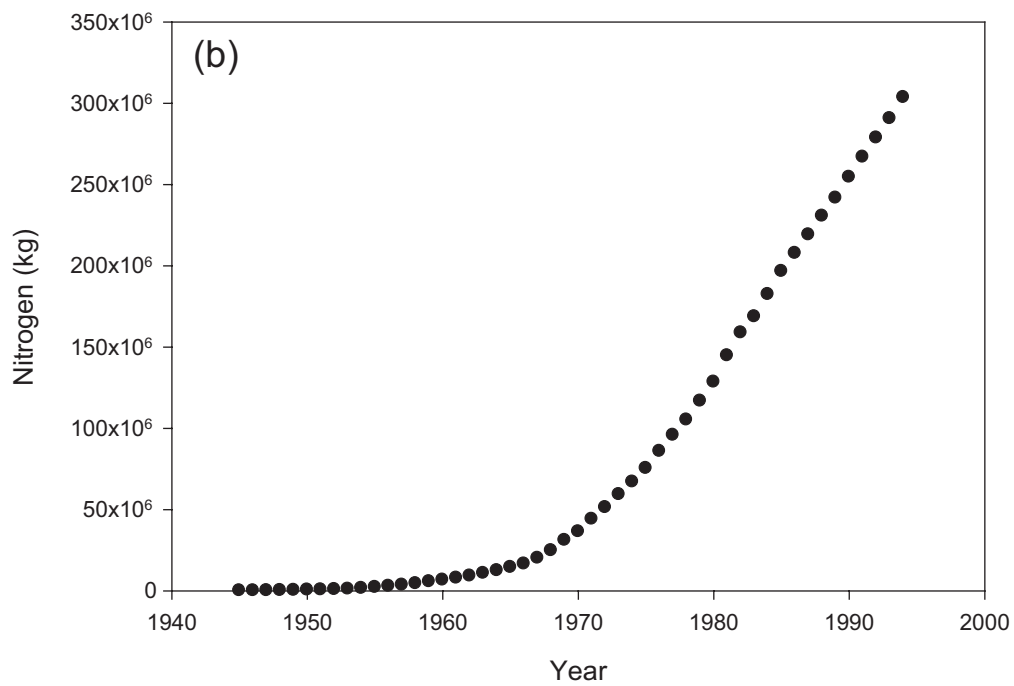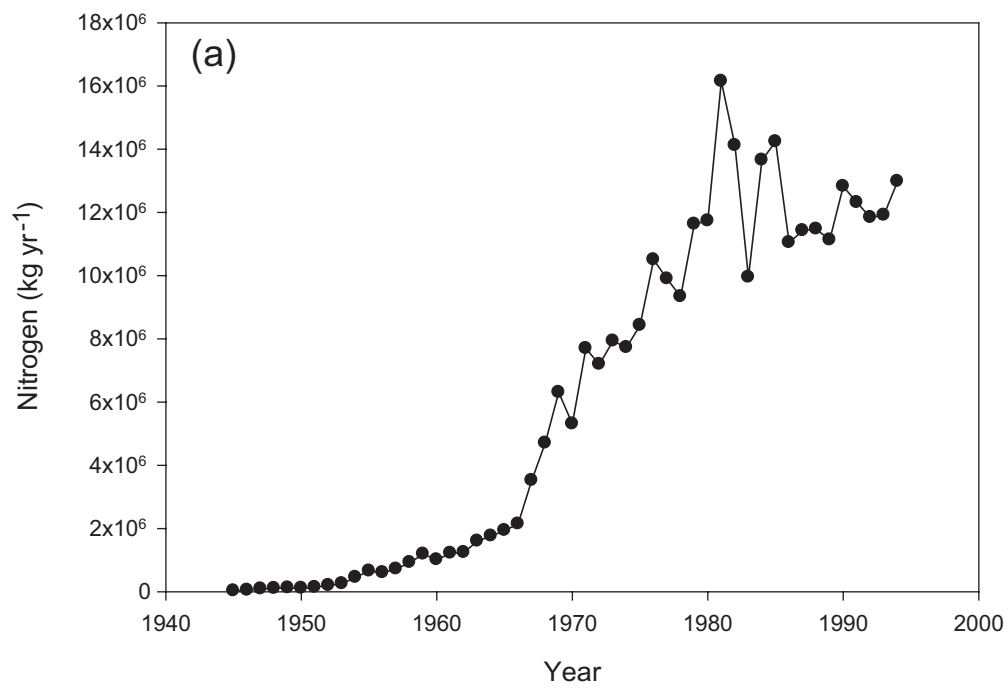
Figure 3. Nitrogen application in commercial fertilizer in Otter Tail County since 1945 (a) on an annual basis, and (b) cumulative inputs during the same period.
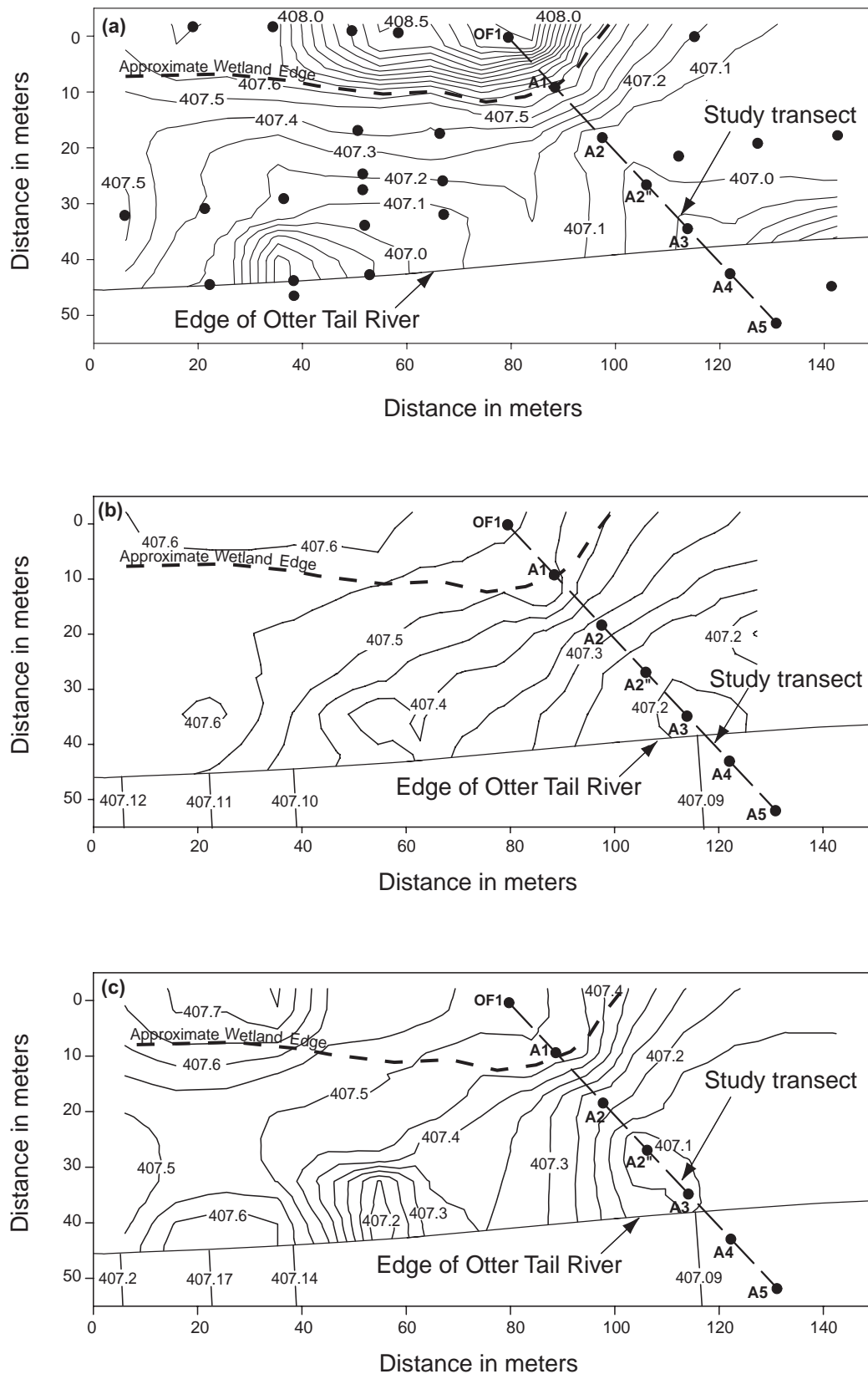
Figure 4. Contour maps showing (a) land surface elevations and locations of sampling points, and (b) and (c) ground-water and river elevations in the 40 m by 140 m study area in the riparian wetland in August 1994 and 1995, respectively. [Individual sample locations are shown as filled circles. Contour intervals are 0.1 m for land-surface elevations, 0.05 m for ground-water elevations, and 0.01 m for river elevations].
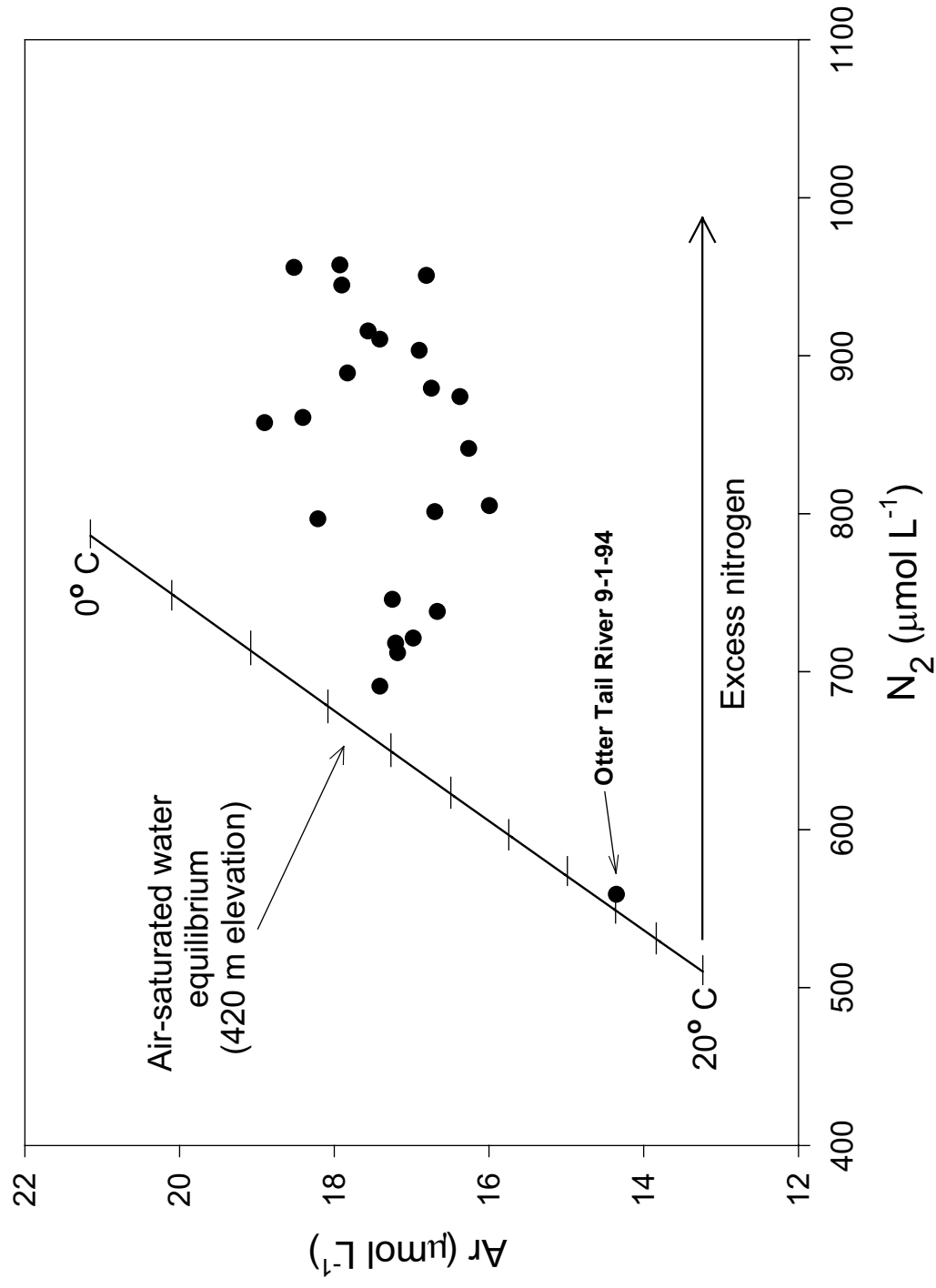
Figure 5. Argon and nitrogen gas concentrations in ground water and their theoretical values assuming air-saturated water equilibrium at 420-m elevation and temperatures ranging from 0° to 20° C. Values to the right of the air-saturated water equilibrium line represent excess nitrogen concentrations. [Horizontal tic marks on the equilibrium line indicate Ar and N_2 equilibrium concentrations from 0° to 20° C in 2° increments].
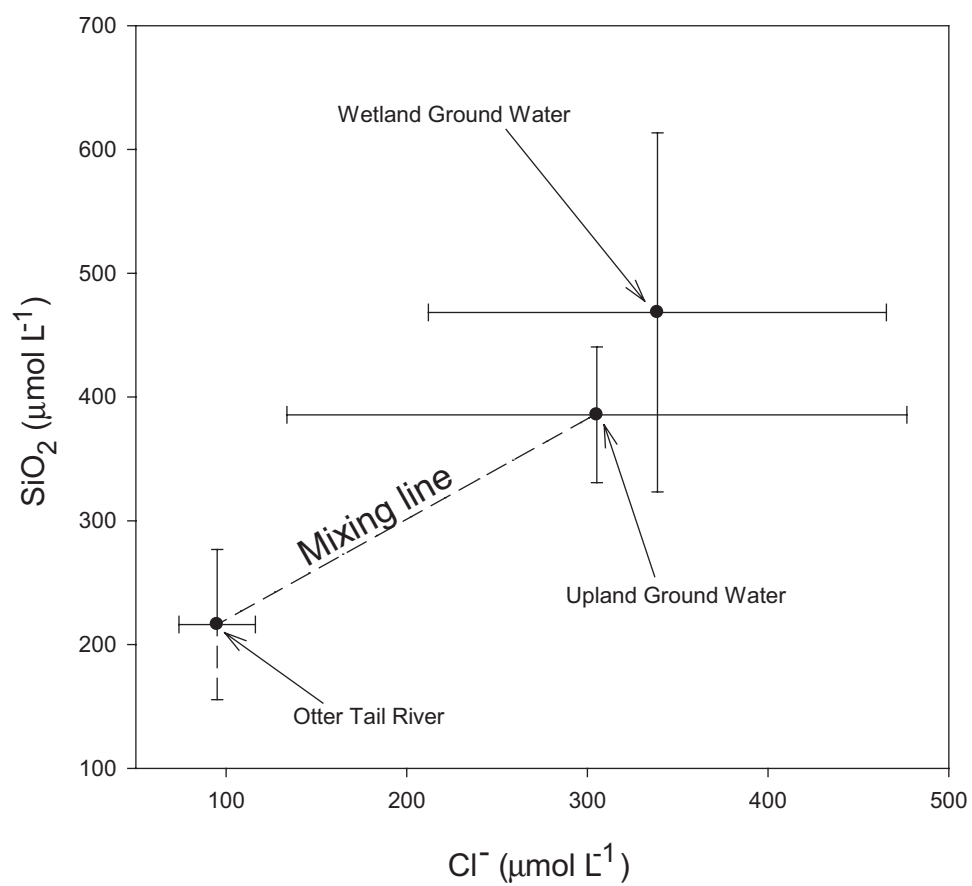
Figure 6. Concentrations of Cl⁻ and SiO₂ in wetland and up-gradient ground waters, and in the Otter Tail River. [Data points are averages and error bars are 1 standard deviation].
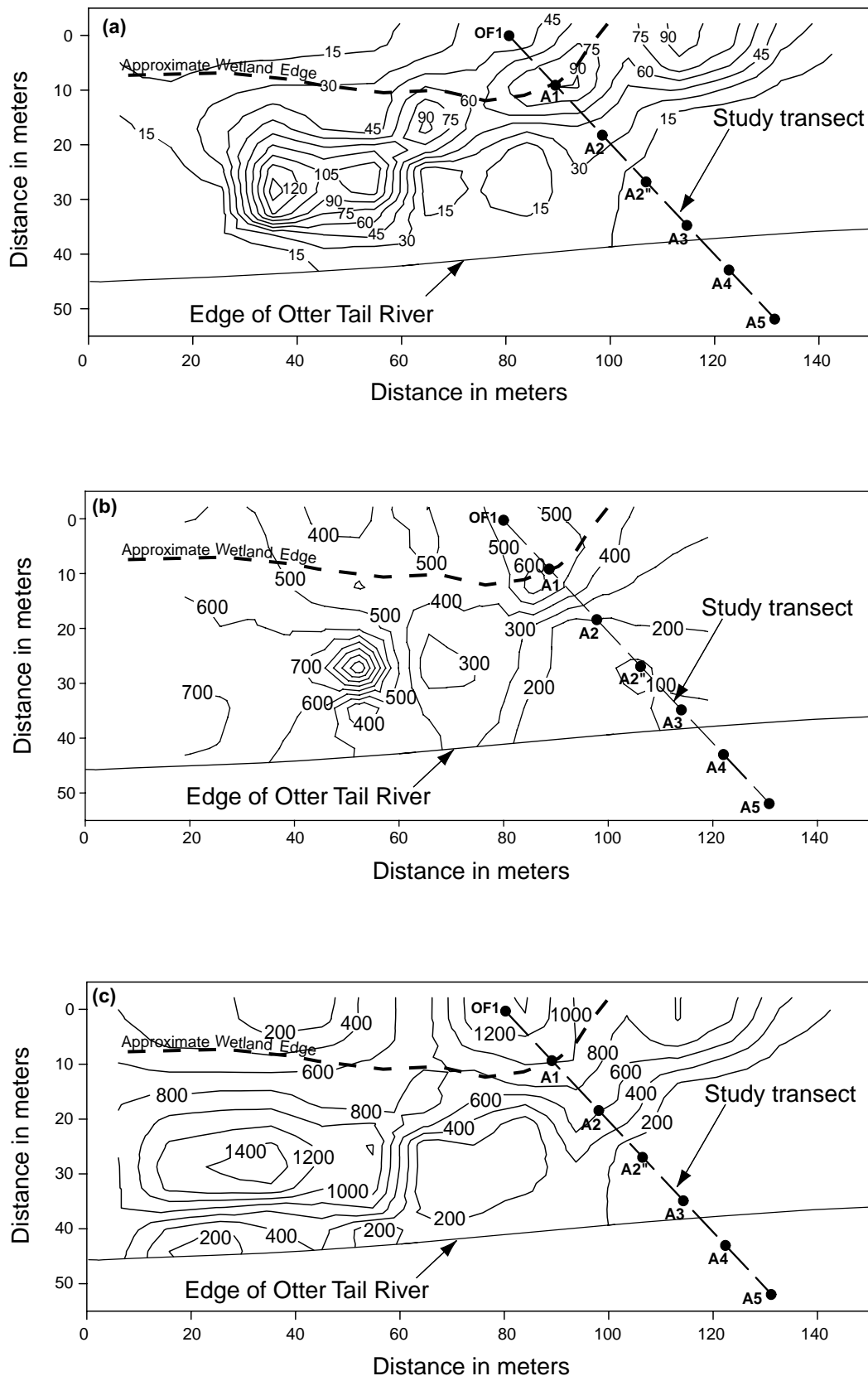
Figure 7. Contour maps showing spatial distribution of (a) dissolved oxygen in August 1995 and (b) and (c) nitrate concentrations in the 40 m by 140 m study area in the riparian wetland in August 1994 and 1995, respectively. [Contour intervals are 15 μmol L^{-1} for dissolved oxygen, 100 μmol L^{-1} for nitrate in 1994, and 200 μmol L^{-1} for nitrate in 1995].
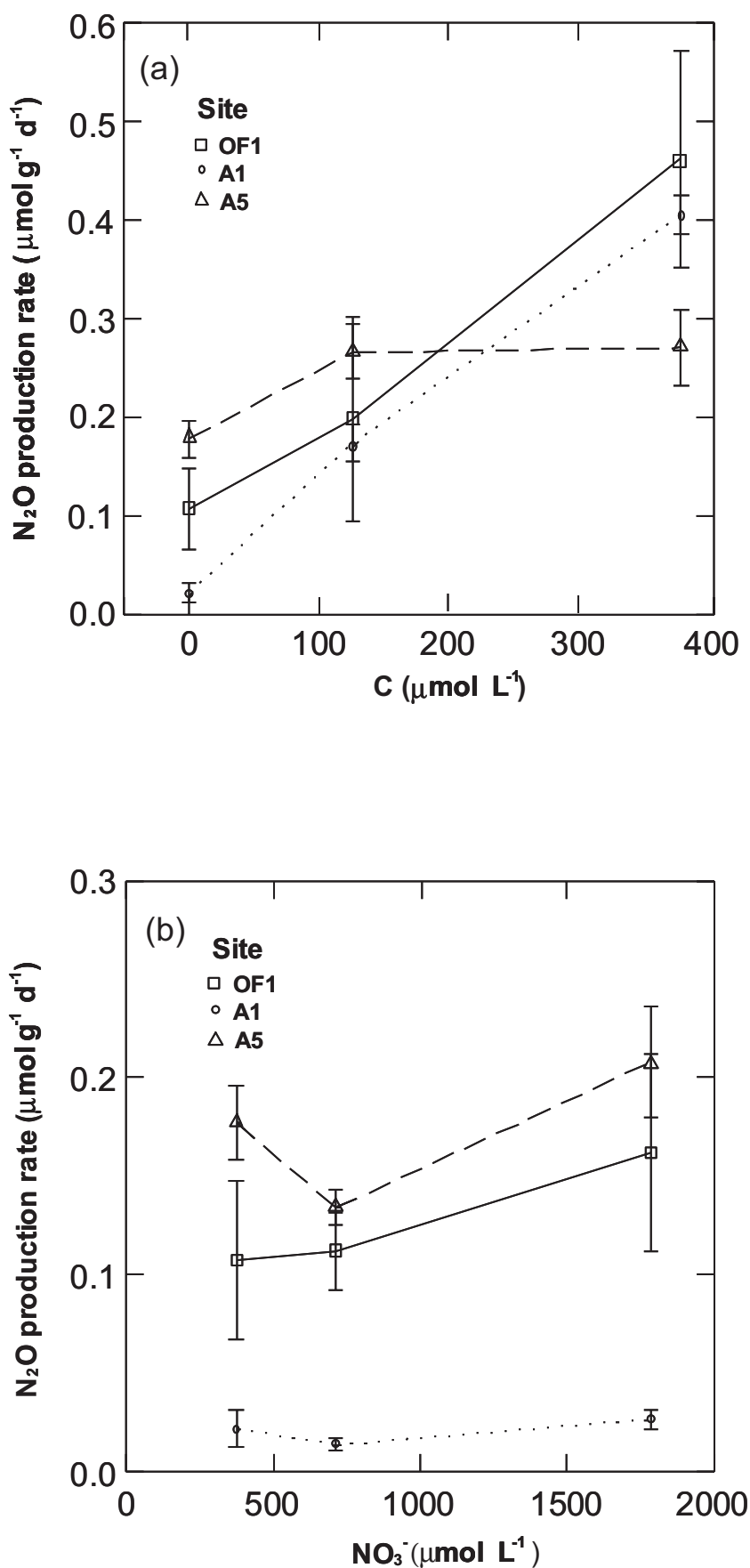
Figure 8. Denitrification rates (expressed as μmol N_2O $g^{-1}d^{-1}$) in response to (a) organic carbon amendments for sediments at OF1, A1, and A5, and (b) NO_3^- amendments for sediments at OF1, A1, and A5 with no additional organic C. [Data points are averages and error bars are 1 standard deviation].
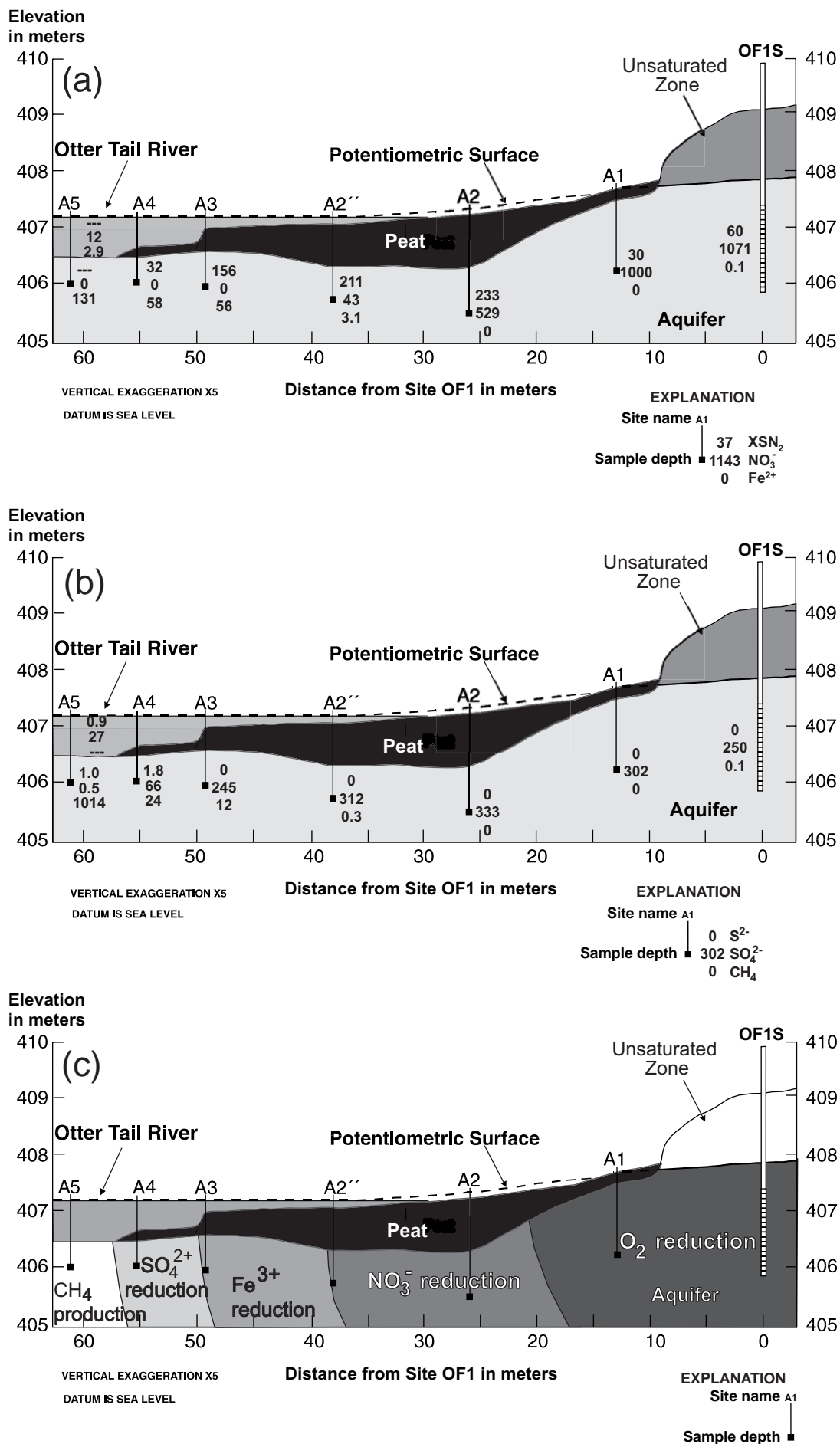
Figure 9. Concentrations of (a) excess N_2 (XS N_2), NO_3^-, and Fe^{2+}, (b) S^{2-}, SO_4^{2-}, and CH_4, and (c) the redox state of ground water along the transect from OF1S-A5. [All concentrations are $\mu mol\ L^{-1}$].

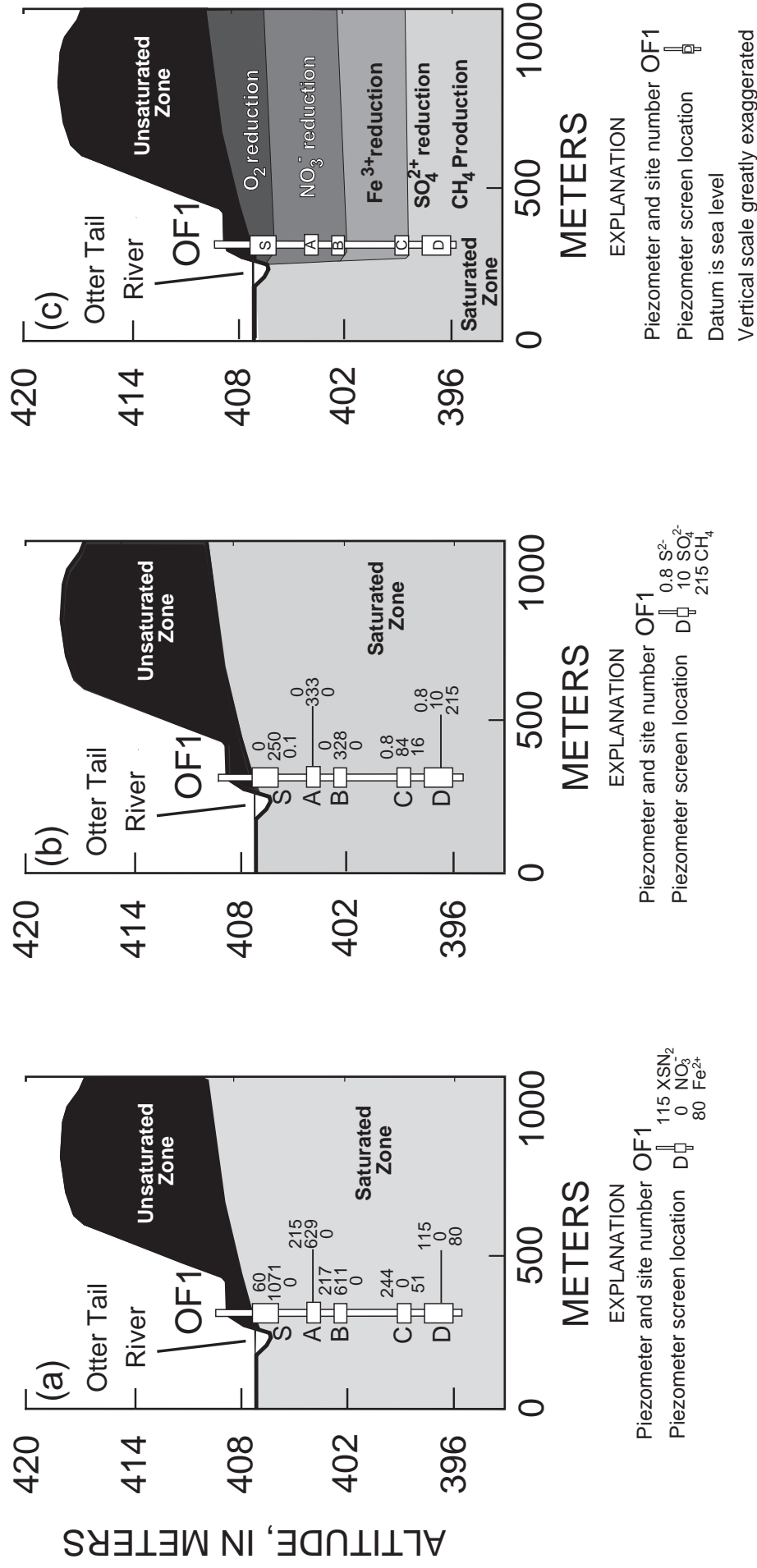Figure 10. Concentrations of (a) excess N_2 (XS N_2), NO_3^-, and Fe^{2+}, (b) S^{2-}, SO_4^{2-}, and CH_4, and (c) the redox state of ground water in the permanent piezometers at site OF1. [All concentrations are $\mu mol\ L^{-1}$].
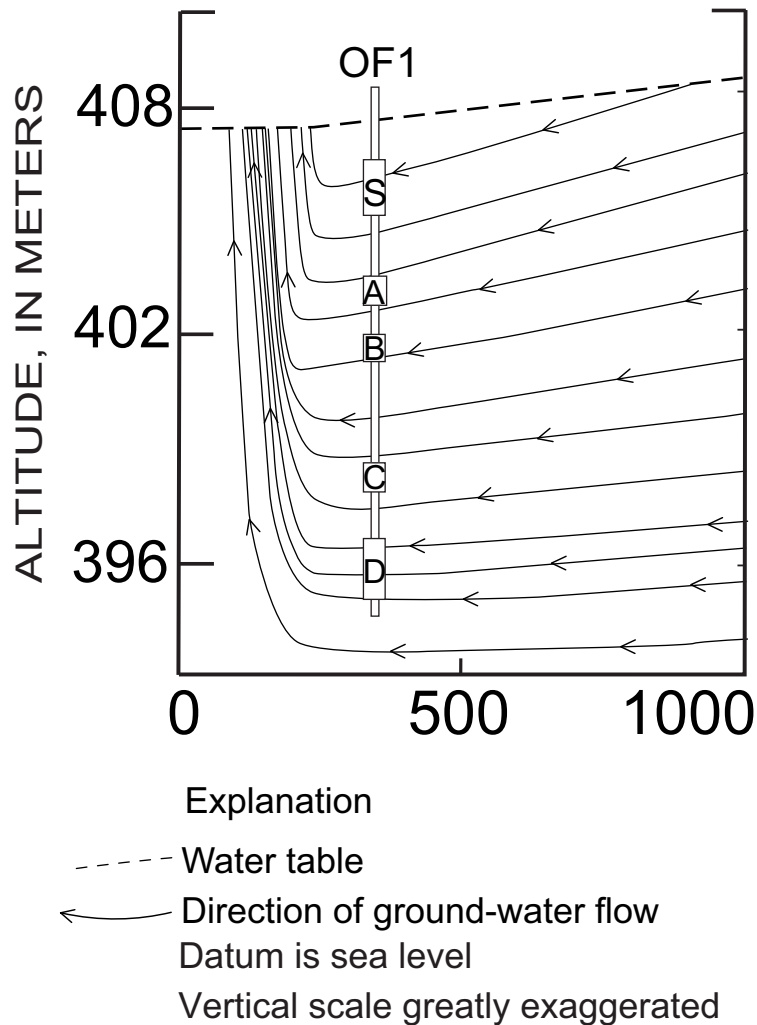
Figure 11. The ground-water flow system for the study area based on results from the Modflow/Modpath ground-water particle-tracking model presented by Puckett and Cowdery (2002). Flow lines reflect the movement of particles originating at various points along the transect and do not represent equal volumes of flow.